POTENTIALS AT METAL-SOLUTION INTERFACES

DISSERTATION

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METHOD OF MEASURING THE ABSOLUTE POTENTIAL OF AQUEOUS HALF-CELLS

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The experimental and theoretical difficulties associated with the absolute potential of single electrodes have led most people to the conclusion that the problems are fundamentally insoluble. In fact, some go so far as to assert that even the concept of such a potential is incapable of thermodynamic expression (8). The purpose of this paper is to present a new method of measuring such potentials, which is based upon the following sequence of ideas: When silver metal is immersed into a solution containing silver ions, the latter, if present in concentrations exceeding a certain critical value, pass from the solution to the metal, until the accumulative positive charge on the metal and the negative charge in the solution stop further transfer of ions. That is to say, an initial potential difference exists between metallic silver and solutions containing silver ions which causes a transfer of matter at the interface, until the so-called Helmholtz layer is formed. If an area of metallic silver sufficiently large to accommodate 1 gram-atom of silver ions in the form of such a layer were brought in contact with a very large volume of solution, it would be possible to write down a numerical value for the energy associated with such a change of state. In this manner, it is possible to characterize thermodynamically a single electrode potential.

The Helmholtz layer may be formed by reactions of the electrode with either cations or anions. For example, if metallic silver be immersed into a solution containing chloride ions, the metal acquires a negative charge owing to the formation of silver chloride, the layer at the interface now consisting of electrons in the metal and the cations initially associated with the chloride ion. The formation of such layers is found to obey the ordinary thermodynamic rules, and definite changes of enthalpy and entropy are associated with such transfers of matter. Furthermore, following the usual criteria of equilibria, it is possible to select a

particular concentration of the aqueous reactive ion such that no layer is formed. A solution of such ion concentration, or partial molar ion entropy, should exhibit zero potential against the metal electrode.

Experimentally a study is made of the transient current between a stationary electrode immersed in an aqueous solution containing a reactive ion and a similar electrode freshly dipped into the same solution. This current and its direction measure the flow of electrons necessary for the formation of the Helmholtz layer. As will be shown, not all electrodes and solutions exhibit these phenomena in such a manner as to allow for the change to be definitely characterized. The changes may be obscured by overlapping kinetic disturbances. If, however, a few or even a single electrode reaction may be formed that answers to a reversible thermodynamic equilibrium, all single potentials may be represented on an absolute scale. It must also be noted that the selection of such a scale, valid for various temperatures, demands a knowledge of the electrode reaction.

The first attempts to find a single potential were those of Lippmann (10) and others with the capillary electrometer and dropping mercury electrode. Later, Bennewitz and Schulz (3) scraped one silver electrode of a pair connected through a galvanometer and observed the direction of current in solutions of different concentrations of silver ion. Bennewitz (2) confirmed his previous value by measuring the interfacial tension of mercury in different concentrations of mercurous nitrate. Billitzer (5) observed the motion of fine metallic particles suspended in a solution subjected to a potential gradient, while Garrison (7) observed the motion of a silver needle under similar conditions. Andauer (1) measured the calomel half-cell potential with a second electrode in the air above the solution.

These direct experimental methods led to one of two values for the single potential of the normal calomel half-cell. The capillary electrometer and dropping electrode gave the value -0.56 v., while the methods of Bennewitz, Billitzer, and Garrison all yielded approximately $+0.19$ v. Andauer reported first one and then the other of these two, widely divergent potentials.

Indirect methods have also been applied to obtain the value of the single potential. For example, a hypothetical mixture of gaseous metal ions, electrons at an energy level lower than gaseous electrons by an amount equal to the work function, and liquid water molecules constitutes an unstable system. Two changes are possible producing more stable states: the ions may unite with the electrons and condense to form the metal, or the ions may neutralize their charge by clustering about themselves the polar water molecules. The single potential is the difference between these two energy paths. All the necessary energy changes are known for the calculation of the single potential except the hydration energy of the ions.

Born (6) has pointed out that the energy of hydration of a gaseous ion should be given by the expression

$$\Delta E = \frac{ze^2}{2r_e} \cdot \frac{D - 1}{D}$$

where r_e is the ion radius and D the dielectric constant. Debye has shown that one would not expect this to hold except where the dielectric does not approach saturation in the vicinity of the ion.

Webb (13) has developed the hydration energy as a sum of the electrical work of charging an ion in a molecular medium plus a term due to the compression of the solvent in the vicinity of an ion. Makishima (11) has used Webb's results to calculate single potentials and reports -0.51 v. for the normal calomel electrode.

Philpot (12), while investigating the nature of the diffuse double layer, calculated a single potential value of silver in 0.1 N sodium chloride as -0.47 v.; this would place the potential of the normal calomel electrode at -0.59 v.

Bernal and Fowler (4) calculated the individual hydration energies of ions in terms of the mutual potential energy of ion and water molecules, the changed orientation of water in the vicinity of an ion, and the energy of the coördination sphere. They assumed that potassium and fluoride ions, having the same radii and the same mutual potential energy, should have the same hydration energy. They then split the known hydration energy of the ion pair and used the value as the starting point for calculating hydration energies of other ions. Although the authors made no calculations of potential, an acceptance of their hydration energies leads to a single potential of $+0.18$ v. for the calomel electrode.

Recently Latimer (9) has shown that the addition of an arbitrary constant to the radii of the positive ions, and another smaller one to the negative ions, leads to agreement with the Born equation with the dielectric constant taken as that of normal water. He then calculated the single potential of the normal calomel electrode to be -0.50 v.

It is curious indeed that all determinations, both theoretical and experimental, have led to normal calomel electrode potentials in agreement with one or another of the two widely separated values -0.56 v. or $+0.19$ v. Nearly all of the methods so far proposed are open to objections. The direct determination by electrocapillary curves will subsequently be shown to be in error, owing to the presence of complex mercuric ions, which have heretofore been lost sight of. The dropping mercury electrode gives erroneous results, owing to its operation under conditions that do not allow the mercury sufficient time to form its equilibrium layer.

The following method has been used to determine the single potential of the calomel electrode: A cathode-ray oscillograph, with triple amplification of the input signal, proved to be satisfactory for the detection of these transient currents. Using this device, deflections were observed for a large number of electrodes, and reversal points were determined for several systems. The potentials of electrodes in solutions of proper concentration for reversal of the direction of deflection were then measured against a calomel half-cell. The overall potential was taken to be the single potential of the calomel electrode. The reversal point with different electrodes occurred at approximately the same potential, though absolute concordance was not obtained.

APPARATUS AND MATERIALS

The cathode-ray oscillograph was an R.C.A. instrument, type T.M.V. 122B. It has been modified for the detection of direct current potentials by a previous

investigator in this laboratory. The essential changes in design are shown in figure 1. The heavy lines are a reproduction of part of the schematic diagrams

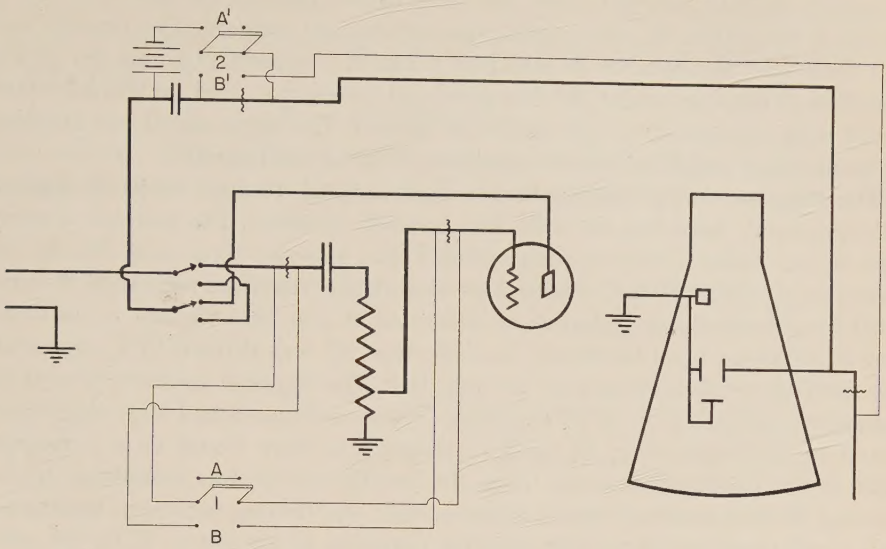

FIG. 1. Diagram of the cathode-ray oscillograph

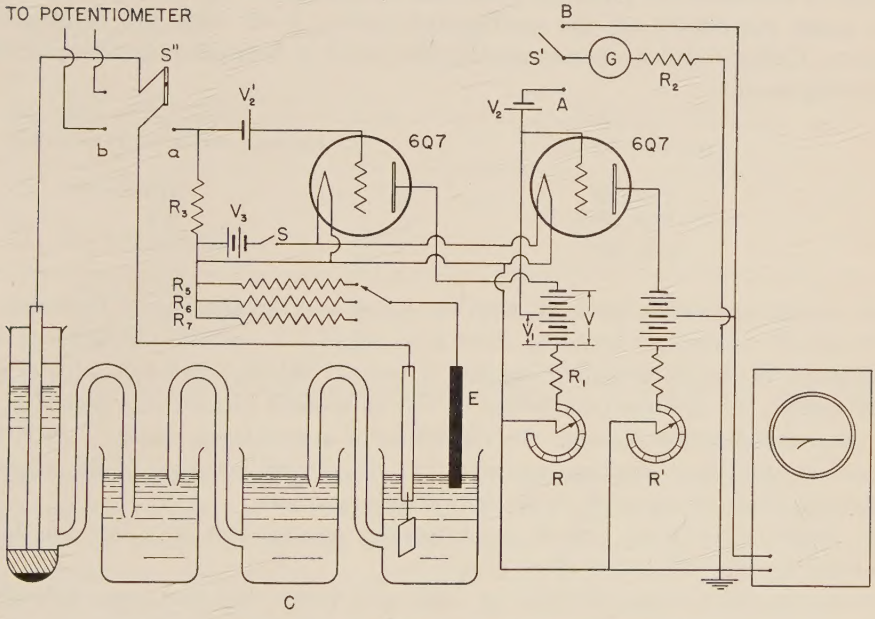

FIG. 2. Complete wiring diagram for the experimental set-up

furnished with the instrument, while the light lines show the modifications introduced. Breaks in the original circuit are shown by wavy lines. When switch 1 is in position A, the condenser and gain control are by-passed. When it is in position

B, the connections are the same as in the original instrument. When switch 2 is in position A′, the vertical beam shift is disconnected and the condenser by-passed. A battery of 180 v. serves to keep the beam in the center of the screen. When the switch is in position B′, the original connections are restored. The present work was done with the switches in positions A and A′, respectively, and the vertical amplifier of the instrument on. The saw-tooth sweep was used on the horizontal plates with a frequency of 120 cycles per second. The input signal was amplified by an auxiliary amplifier before connection with the oscillograph.

The complete wiring diagram for the experimental set-up is shown in figure 2. All equipment, including the cells, was carefully shielded. The method of operation was as follows: After closing switch S and allowing some time for the filaments to get hot, switch S′ was thrown to position A and the resistance R varied until the galvanometer G showed no deflection. S′ was then thrown to position B and R′ adjusted until G showed no deflection. S″ was thrown to a, connecting the fixed electrode to the grid of the amplifier. The identical electrode E could be connected through 2, 5, or 10 megohms. These resistances had to be large compared to that connecting the grid to ground, or there would be a permanent shift of the oscillograph beam when the parallel circuit was completed by immersing E. This indicated that a slight current was flowing between filament and grid at all times in spite of the negative potential of the latter. With the ratios shown, however, no permanent shift could be detected; yet the deflections produced by electrodes far removed from the reversal point were sufficient to throw the beam completely off the oscillograph screen, even with the 10-megohm resistor. Calibration with permanent applied E.M.F.'s between a and E gave the following results:

RESISTANCE IN OHMS	MILLIVOLTS PER MILLIMETER DEFLECTION
2×10^6	1.0
5×10^6	2.3
10×10^6	4.5

This varied somewhat, however, with the aging and replacement of batteries.

Switch S″ of figure 2 could be thrown to position b and the potential of the stationary electrode measured against a normal calomel half-cell with a potentiometer. An intermediate bridge of 1 *N* potassium nitrate was placed at C to prevent difficulties through the formation of insoluble chlorides. This introduced an additional junction potential, but the overall accuracy of the method did not justify any attempts to determine its magnitude.

A Leeds & Northrup type K potentiometer was used at first, but was later replaced by the ordinary student type.

Solutions were prepared with C.P. salts and water that had been redistilled from a phosphoric acid–potassium permanganate mixture in a Pyrex still. Since the solutions had to stand many hours in glass during the course of a determination, no further precautions were deemed worth while.

Electrodes were prepared from the purest metals obtainable and always from

the same piece to avoid permanent differences of potential due to different structure or differing amounts of impurities. In all cases where a reversal of deflection was observed with a given metal, four or five electrodes were used, with frequent exchanges of stationary and moving electrodes to assure that no spurious reversal was being observed.

EXPERIMENTAL

The validity of the method was first tested qualitatively by observing the deflections of silver electrodes in strong silver nitrate solution and zinc electrodes

TABLE 1

Current deflections between moving and stationary electrodes

SYSTEM	REVERSAL POINT E_H
Zn, Zn^{++}	No reversal; electrode always negative
Cd, Cd^{++}	No reversal; electrode always negative (?)*
Tl, Tl^{+}	No reversal; electrode always negative
Co, Co^{++}	No reversal; electrode always negative
Ni, Ni^{++}	No reversal; electrode always positive
Sn, Sn^{++}	No reversal; electrode always negative
Pb, Pb^{++},	No reversal; electrode usually negative (?)
Cu, Cu^{++}	No reversal; electrode always positive
	volts
Ag, Ag_2O, NH_4OH	-0.46 ± 0.01
Ag, $AgIO_3$(s), KIO_3	-0.47 ± 0.01
Au or Pt, Fe^{++}, Fe^{+++}, SO_4^{--} H^{+}	-0.47 ± 0.01
Au or Pt, quinhydrone, H^{+}, Na^{+}, CH_3COO^{-}	-0.47 ± 0.01
Au, $K_4Fe(CN)_6$ / $K_3Fe(CN)_6$ KNO_3	-0.46 ± 0.01

* The (?) on the cadmium and lead systems indicates that the results were occasionally erratic.

in zinc sulfate solution. One electrode of the metal under consideration was immersed and connected to the high side of the amplifier. Another identical electrode was connected through the 10-megohm resistance to ground and suddenly dipped into the solution. In agreement with the initial hypothesis, the observed oscillograph deflections were in opposite directions and in accord with the charge one might expect to be present on the stationary electrode, i.e., as if zinc acquired a negative charge in solution and silver a positive charge. The deflections died out rapidly in both cases, a single sweep being sufficient for most of the potential difference to disappear.

Following this encouraging result a large number of electrode systems (see table 1) were investigated in an attempt to find those that would show a reversal of deflection with change in solution concentration. When such a system was found, the stationary electrode was used as one electrode of a cell having a normal calomel electrode as the other terminal and the overall potential was measured with the potentiometer.

Certain characteristics of behavior were found to be common to nearly all of the systems studied. The speed of immersion or the area touching the solution had no observable effect on the magnitude or duration of the deflection. A sudden increase in the interfacial area after the initial immersion would cause a slight momentary deflection, but of much lower magnitude than that observed initially. Shaking an electrode caused "motor electric" potentials that were much smaller than the deflection on immersion. Some electrodes such as nickel and cobalt gave relatively permanent residual potential differences, due undoubtedly to their hardness and apparent lack of reversibility. All systems except those reversible to anions showed relatively permanent deflections when the concentration of metal ion dropped below 10^{-5} M. In solutions approaching saturation in fairly soluble salts the deflections frequently could not be detected. With zinc, however, deflections were readily apparent even in saturated solution.

ELECTRODE SYSTEMS STUDIED

The Zn–$ZnSO_4$ *couple*

Cast zinc electrodes were rubbed with fine emery before use. In all concentrations of zinc ion deflections were very strong, the beam being thrown completely off the screen. Return to the original base line was rapid in solutions stronger than 10^{-5} M, being complete in one or two sweeps of the oscillograph. Highly diluted solutions led to smaller residual potential differences after the initial large deflection that would sometimes require nearly a minute to die out. The large jump was always in such a direction as to indicate a negative charge in the stationary electrode, but residual potentials were erratic, lying on either side of the base line. Heating an electrode before use to assure a heavy oxide coating had no effect upon the nature of the deflection.

The Cd–$Cd(NO_3)_2$ *couple*

Cast cadmium electrodes buffed with emery were also used in this determination. In solutions of concentration less than 1 N there was a rapid deflection indicating a negative charge on the stationary electrode, followed immediately by a relatively permanent potential difference of opposite sign that died out slowly. As the solution was made more concentrated, the initial deflection of opposite sign was apparent. This die-out constitutes an actual reversal, since there was no growth of a *rapid* deflection of opposite sign. The indication was merely that high concentration permitted adjustment of potential more rapidly than the oscillograph could follow.

The Tl–$TlC_2H_3O_2$ *couple*

This system was tried only in 1 N solution. Deflections were always such as to indicate a negative charge on the stationary electrode.

The Co–$CoSO_4$ *couple*

Tested in 0.1 N, 1.0 N, and saturated solutions this couple always showed a negative charge. Return to equilibrium was always rapid, yet the potential in saturated solution was $E_H = +0.200$ v., a value far from the reversible potential.

The Ni–$NiSO_4$ *couple*

Nickel electrodes were prepared from heavy nickel wire and buffed with emery before use. The potential of such an electrode in 1 N nickel sulfate was found to be $E_H = -0.07$ v., a value far more noble than the reversible potential. Deflections also were relatively permanent, lasting 15–20 min. before equilibrium was attained. In all cases deflections were in such direction as to indicate a positive charge. Owing to the apparent irreversibility of this system the positive potential was not considered significant.

The $Sn–Sn^{++}$ *couple*

Both stannous chloride in hydrochloric acid and stannous perchlorate were used as test solutions. In all concentrations tin electrodes showed a consistently negative charge.

The Pb–$Pb(NO_3)_2$ *couple*

Erratic results were obtained with this system. Emery-buffed electrodes sometimes made the stationary electrode appear positively charged, while those that were merely washed and wiped briskly with a towel gave the opposite effect. This was the first evidence that the preliminary treatment of the dipping electrode could alter the result obtained. It was not consistent in the case of lead, however. Regardless of treatment of the dipping electrode, the stationary one appeared negative about 80 per cent of the time. No method could be devised to eliminate the variability of this soft metal and produce a reproducible surface, so experiments were discontinued.

The $Ag–Ag^+$ *couple*

This system was first tested in silver iodide–potassium iodide solution because the potential could be raised above that of lead. Silver iodide was precipitated from silver nitrate with potassium iodide and, after washing, was left in distilled water for 2 weeks. Crystals of potassium iodide were dissolved in this solution before use. In spite of the low silver-ion concentration, equilibrium was established rapidly as long as the iodide-ion concentration was reasonably high. Apparently the system behaved reversibly with respect to iodide ion, even though the electrodes were initially free of silver iodide.

Silver electrodes were prepared from heavy silver wire. The wire was covered with a thin oxide layer when first obtained. This was reduced by heating in a

flame to a dull red heat, leaving a white layer of silver on the electrode. After being used once, the electrodes were washed in distilled water and then dipped in nitric acid to remove any iodide remaining on the surface. A second washing, followed by heating, restored a pure silver surface.

Deflections indicated that the stationary electrode was negatively charged in all concentrations of iodide ion. This served to confirm the opinion that silver was probably negatively charged.

Silver electrodes were then tried in silver chloride–1 *N* chloride and finally in 0.1 *N* silver nitrate. The stationary electrode was negatively charged in the former solution and positively charged in the latter. This indicated definitely that a reversal point lay somewhere between these extremes.

A semisaturated silver oxide solution, prepared by boiling silver oxide in water for 20 min., was found to charge silver positively. The potential initially was $E_H = -0.59$ v. Dilute ammonia solution was added drop by drop and the deflections observed. In this experiment electrodes were reactivated by heating to red heat only, since the substances forming the ion layer are all decomposed or driven off by heat. In addition to the rapid initial deflection there was always a small residual potential difference that interfered with observation as the principal deflection became smaller. Nevertheless it was possible to observe a definite reversal of direction of deflection in the potential range $E_H = -0.45$ to -0.47 v.

Since the above solution was essentially the same as that used by Bennewitz and Schulz, who report the same reversal point, it appeared desirable to select one in which total salt concentration would be higher and thus eliminate the possible objection that deflections might be due to a zeta potential. A reversal was obtained successfully in a solution containing silver iodate and potassium iodate, although it was more difficult to observe because of relatively large, permanent potential differences. The potential at reversal appeared to lie in the range $E_H = -0.47$ to -0.48 v.

The Hg–Hg_2^{++} *couple*

Gold wires were fused to a bead on the tip and sealed into glass tubing. The beads were dipped into mercury that had been purified with great care. The amalgamated beads so obtained were transferred rapidly from mercury vessel to test solution to avoid as much as possible the formation of oxide and diffusion of gold to the surface. The solutions tested were mercurous chloride–potassium chloride, mercurous iodide–potassium iodide, and mercurous bromide–potassium bromide. The halides gave uniform deflections in such a direction as to indicate that the stationary electrode was positively charged. Even in a solution saturated with potassium iodide the deflection was not changed.

The Fe^{++}–Fe^{+++} *couple*

A solution of ferrous ammonium sulfate was acidified with sulfuric acid and left in contact with zinc for a few minutes to ensure removal of oxidized iron. A large gold foil was used as the stationary electrode and No. 22 gold wire as the dipping

electrode. Some difficulty was encountered in the reactivation of such electrodes after use. Heating in a flame to redness leaves no appreciable layer of finely divided gold, as in the case with silver or copper in hydrogen. Attempts to use this method without modification led to fast fleeting deflections, too fast for the camera to record, which were in such direction as to indicate that the stationary electrode was negatively charged down to a potential of $E_H = -0.73$ v., attained by adding first ferric sulfate and finally potassium dichromate. Since these were not full-bodied deflections, such as had been obtained previously, a study was made of the effect of different electrode treatment. As with other metals, scratching with emery raised the potential at reversal to a value above that for silver. Washing and wiping without heating gave a reversal at -0.47 v., in agreement with silver, but the possibility of ions from the solution being retained was too great to justify this procedure. To remove adsorbed ions the electrodes were washed, dipped in aqua regia, rinsed, heated to redness, and then rubbed gently on a soft cloth. This sufficed to insure a clean surface that was unscratched and yet the fleeting deflections were overcome. With this treatment the reversal point lay between -0.47 and -0.48 v.

The reversal with this system could be attained from either side by using stannous chloride to raise the potential after lowering with ferric sulfate. The presence of stannous chloride caused some semipermanent potential difference, however, that tended to obscure the exact point of reversal when changing toward less noble potentials.

The quinone–hydroquinone | gold couple

A saturated water solution of quinhydrone was acidified with acetic acid, and sodium acetate was used to lower the hydrogen-ion concentration. Reversal of deflection occurred at -0.47 ± 0.01 v. There was very little base-line shift with this system, equilibrium being attained quite rapidly. In any single determination it appeared possible to place the reversal point within a few millivolts, yet there was enough fluctuation between successive determinations and between different gold electrodes to introduce a greater degree of uncertainty. Platinum electrodes yielded essentially the same reversal point, but more often gave semipermanent potential differences that made observation difficult.

The $Fe(CN)_6^{4-}$–$Fe(CN)_6^{3-}$ | Au *couple*

A 1 N potassium nitrate solution was used as a supporting electrolyte in this determination; 0.1 N solutions of potassium ferrocyanide were added in small amounts, 0.5–1.0 ml. to 30 ml. of the potassium nitrate solution. The reversal point was established at $E_H = -0.46 \pm 0.01$ v. This system was the most perfect one studied from the standpoint of rapid attainment of equilibrium. Reversal could be obtained by shifting the potential in either direction, and great accuracy was prevented only by lack of a perfectly reproducible method of reactivating electrodes. A typical set of photographs of deflections is shown in figure 3. They illustrate the gradual decrease in magnitude of deflection with change in the potential, the shift through zero, and the build-up on the opposite side.

The behavior of fresh mercury surfaces against halide solutions appears anomalous, for, from the absolute potential of the calomel solution (+0.19 v.), one should expect a negative charge on the metal. However, the initial transient current as detected by the oscillograph indicates a positive charge on the mercury. This action may be explained by assuming the initial effect to be a reduction of the adsorbed mercury complexes which is subsequently followed by a slower

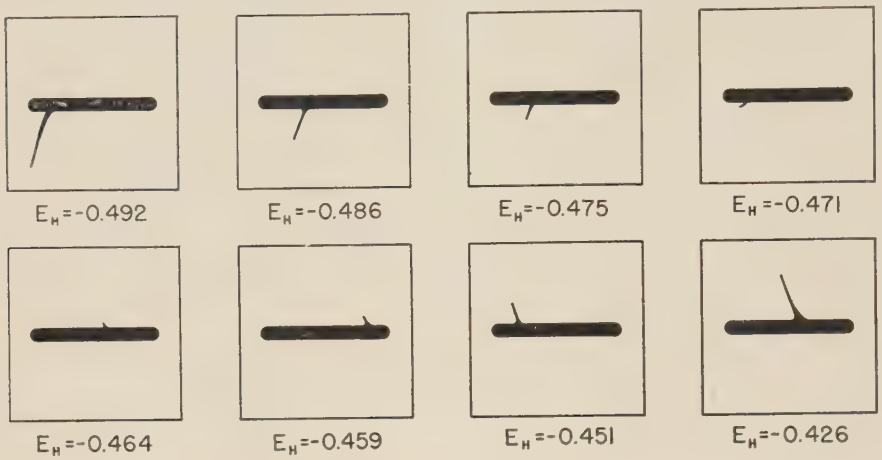

FIG. 3. Typical set of photographs of deflections

re-formation of the same. The situation may be approximated by means of the following equilibria:

$$Hg_2Cl_2 \rightleftarrows Hg_2^{++} + 2Cl^- \qquad K = 1.1 \times 10^{-18}$$

$$Hg_2^{++} \rightleftarrows Hg + Hg^{++} \qquad K = 1/80$$

$$HgCl_4^{--} \rightleftarrows Hg^{++} + 4Cl^- \qquad K = 1 \times 10^{-16}$$

from which it follows that the $HgCl_4^{--}$ ion concentration in 1 N calomel solution is of the order of 10^{-4} mole per liter. It is to be noted that the latter concentration is 10^{14} times as great as the mercurous-ion concentration. In the adsorbed layer of the complex the initial reduction must take place, and this reduction is indicated by the oscillograph.

The presence of such high concentrations of the mercuric complexes is also responsible for the failure of the capillary electrometer to measure absolute potentials correctly. This latter instrument is essentially a concentration cell with diminishing concentration of the mercury complex in the capillary as the polarization potential is increased. An accurate evaluation of the effect would require an exact knowledge of the stability of the complexes as well as the transference numbers of the same. In other words, one should know whether the complex is $HgCl_3^-$, $HgCl_4^{--}$, or $HgCl_5^{---}$, etc., the equilibrium concentrations, and their transference numbers before one could evaluate the potential of the concen-

tration cell. It is hardly necessary to say that such knowledge is not available at present; furthermore such data are unnecessary, as long as we realize that the potential applied to a capillary electrometer does something more than merely change the interfacial surface energy. The latter change is associated with the reduction in concentration of the mercury complex. It is incorrect to assume that the electrical energy is equal to the change in surface energy.

The method used for obtaining the zero point in the present work appears to be less objectionable than any that has been employed heretofore. In addition, the results agree with the theoretical work, which has taken the most detailed account of the structure of the solvent medium. The results do not agree with the theoretical results of Born and Webb, both of whom treat the solvent as a continuous dielectric medium of unchanging properties. On the basis of the cited facts it is probable that the zero of single potentials actually lies near $E_H = +0.47$ v. rather than at $E_H = +0.28$ v., the value that has been most commonly accepted in the past.

There are two major objections that appear if one tries to interpret the present results as manifestations of electrokinetic potential: first, the magnitude of the deflections; second, the wide range of electrolyte concentrations used. With any electrode far removed from the reversal point the deflections indicate potential differences that are much greater than any known electrokinetic potentials. Furthermore the solution may greatly vary in ionic strength, with no apparent effect upon the reversal point. Electrokinetic potentials, on the other hand, are most sensitive to variation of ionic strength, practically disappearing in concentrated electrolyte solutions.

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VITA

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